

## Complexation and Exchange Reactions of some Dimethylamino-substituted Group 4 Compounds

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Reactions of  $\text{CH}_2(\text{NMe}_2)_2$ , (1),  $\text{SiMe}_2(\text{NMe}_2)_2$ , (2),  $[\text{Ti}(\text{cp})(\text{NMe}_2)_3]$  (cp =  $\eta$ -cyclopentadienyl), (3), and  $[\text{Zr}(\text{cp})_2(\text{NMe}_2)_2]$ , (4), with covalent metal halides  $\text{MCl}_4$  (M = Ti, Zr, Hf, Si, Ge, or Sn) and  $\text{MCl}_3$  (M = Ti, V, or Cr) fall into two categories: (a) *N*-donor chelation leading to complex formation and (b) halide– $\text{NMe}_2$  exchange. Compound (1) gives 1 : 1 complexes with  $\text{MCl}_4$  (M = Ti or Sn) and a 2 : 1 complex with  $\text{VCl}_3$ . Compound (2) provides 1 : 1 complexes with  $\text{MCl}_4$  (M = Ti, Zr, Hf, or Sn). The decomposition of  $\text{TiCl}_4 \cdot \text{SiMe}_2(\text{NMe}_2)_2 \longrightarrow [\text{TiCl}_3(\text{NMe}_2)]$  invariably occurs in both the solid state and solution. There is no reaction of (2) with metal(III) chlorides. With  $\text{MCl}_4$  (M = Si or Ge) 'scrambling' reactions involving halide– $\text{NMe}_2$  exchange occur and these have been monitored by  $^1\text{H}$  n.m.r. spectroscopy. Reactions of (3) and (4) with  $\text{MCl}_4$  (M = Si, Ge, Sn, Ti, Zr, or Hf) consistently feature halide– $\text{NMe}_2$  exchange rather than adduct formation. All complexes have been characterised by analytical and spectroscopic ( $^1\text{H}$  n.m.r. and i.r.) investigations.

AMIDES of Group 4 with a direct  $\text{M}-\text{NR}_2$  linkage exhibit a wide range of chemical behaviour. Characteristically they are poor Lewis bases. Loss of electron density at nitrogen through internal  $p_\pi-d_\pi$  bonding weakens their donor capacity compared with the carbon analogues as demonstrated by various spectroscopic<sup>1</sup> and calorimetric<sup>2</sup> data. Facile bond cleavage of the metal–nitrogen bond with *e.g.* protic reagents<sup>3–5</sup> and the many exchange reactions involving group redistribution or 'scrambling' with metal or metalloidal halides<sup>6–8</sup> add a further complication by severely restricting the choice of reference Lewis acid.

Early co-ordination studies with dimethylamino-substituted silanes provided several 1 : 1 complexes with the soft Lewis acids  $\text{B}_2\text{H}_6$  and  $\text{MMe}_3$  (M = B, Al, or Ga); in general these were found to be thermally unstable with complete decomposition at room temperature.<sup>9,10</sup> Adduct formation between  $\text{SiMe}_x(\text{NMe}_2)_{4-x}$  ( $x = 1$  or  $2$ ) and the hard acids  $\text{MCl}_4$  (M = Sn, Ti, or Zr) and  $\text{VOCl}_3$  is reported, although detailed characterisation is lacking.<sup>11</sup> Cyclic silicon amines  $(\text{Me}_2\text{Si}-\text{NH})_x$  ( $x = 3$  or  $4$ ) give a series of 1 : 1 and 1 : 2 complexes with  $\text{TiCl}_4$  and  $\text{MCl}_3$  (M = Ti, V, or Cr).<sup>12</sup> The chelate ligands L,  $\text{Me}_2\text{X}^-\text{M}'\text{Me}_2\text{CH}_2\text{X}'\text{Me}_2$  (X, X' = N, P, or As; M' = Si or Ge), provide a range of  $[\text{M}(\text{CO})_4\text{L}]$  complexes (M = Cr, Mo, or W) involving X, X' co-ordination to the metal.<sup>13</sup> The compounds  $\text{M}(\text{NMe}_2)_4$  (M = Sn or Ti) form 1 : 1 complexes with  $\text{SnCl}_4$  but details are scant.<sup>11</sup> Reaction of  $\text{Sn}(\text{NR}_2)_2$  with an excess of  $\text{BF}_3$  gives the recently reported  $\text{Sn}(\text{NR}_2)_2 \cdot 3\text{BF}_3$ .<sup>14</sup> Perhaps the best characterised Group 4A amide complexes involve the monomeric  $[\text{M}(\text{CO})_3\{\text{Ti}(\text{cp})(\text{NMe}_2)_3\}]$  (M = Cr, Mo, or W) (cp =  $\eta$ -cyclopentadienyl) in which the titanium amide acts as a terdentate *N*-donor.<sup>15</sup> Herein we report our studies of the chelate co-ordination behaviour of a selection of dimethylamino-substituted compounds of Groups 4A and 4B.

### EXPERIMENTAL

Solvents were distilled under nitrogen from either  $\text{CaH}_2$  or  $\text{P}_2\text{O}_5$  prior to use. Anhydrous metal chlorides and  $\text{CH}_2(\text{NMe}_2)_2$ , (1), were used as supplied commercially.  $\text{SiMe}_2(\text{NMe}_2)_2$ , (2), was obtained from direct dimethylamino-lysis of  $\text{SiMe}_2\text{Cl}_2$  in *n*-hexane.  $[\text{Ti}(\text{cp})(\text{NMe}_2)_3]$ , (3), was isolated as a deep red semi-crystalline solid (36% yield) from lithioaminolysis of  $[\text{Ti}(\text{cp})_2\text{Cl}_2]$  in *n*-hexane–toluene. The 'expected' product of the reaction,  $[\text{Ti}(\text{cp})_2(\text{NMe}_2)_2]$ , obtained by Chandra and Lappert<sup>4</sup> *via* the same route under similar reaction conditions was not detected.  $[\text{Zr}(\text{cp})_2(\text{NMe}_2)_2]$ , (4), was prepared by the literature method.<sup>4</sup>

Infrared spectra were recorded on a Perkin-Elmer 580B spectrophotometer with samples as Nujol and hydrocarbon mulls sandwiched between CsI plates. Hydrogen-1 n.m.r. spectra were obtained using a Perkin-Elmer R34 (220-MHz) spectrometer with  $\text{C}_6\text{D}_6$  or  $\text{CD}_3\text{NO}_2$  solutions ( $\text{SiMe}_4$  as internal standard).

Complexes were prepared under an inert atmosphere of nitrogen by dropwise addition of benzene solutions of the appropriate metal halide to a solution of the ligand, also in benzene. In a typical reaction  $\text{SnCl}_4$  (1 cm<sup>3</sup>, 8.5 mmol) was slowly added to  $\text{SiMe}_2(\text{NMe}_2)_2$  (1.5 cm<sup>3</sup>, 8.5 mmol) to give an immediate white precipitate of  $\text{SnCl}_4 \cdot \text{SiMe}_2(\text{NMe}_2)_2$ . The product was collected, washed with benzene and *n*-hexane, and purified by vacuum sublimation (3.1 g, 91%). Satisfactory microanalyses were obtained for all complexes.

### RESULTS AND DISCUSSION

$\text{CH}_2(\text{NMe}_2)_2$ , (1).—Dropwise addition of (1) to equimolar amounts of  $\text{MCl}_4$  (M = Ti or Sn) in benzene provided the yellow (M = Ti) and white (M = Sn) 1 : 1 adducts in almost quantitative yield. No further reaction occurs with an excess of ligand. The complexes, which are extremely sensitive to hydrolysis, show limited solubility in organic solvents. Analytical and spectral data indicate a *cis*-octahedral chelated structure (Figure 1). Ligand bands in the i.r. spectrum at 1058 [ $\nu(\text{NC}_2)_{\text{asym}}$ ] and 868 [ $\nu(\text{NC}_2)_{\text{sym}}$ ] cm<sup>-1</sup> shift to lower energy: *e.g.*, for M = Ti,  $\nu(\text{NC}_2)_{\text{asym}}$  1041, 991, 952 cm<sup>-1</sup>;  $\nu(\text{NC}_2)_{\text{sym}}$

860, 813  $\text{cm}^{-1}$ , while the distinctive 1383  $\text{cm}^{-1}$  ( $\text{CH}_2$  deformation) band<sup>16</sup> experiences a shift to higher energy (70–75  $\text{cm}^{-1}$ ) on complexation. Separate intense  $\nu(\text{M}-\text{Cl})$  bands at 397, 379, 356, 332 ( $\text{M} = \text{Ti}$ ) and 337, 319 ( $\text{M} = \text{Sn}$ ) support the proposed *cis* formulation. A single  $\text{NMe}_2$  signal  $\delta$  2.80 [(1),  $\delta$  2.10] in the  $^1\text{H}$  n.m.r. spectrum ( $\text{M} = \text{Sn}$ ) confirms equivalent *N*-donor sites. Previous investigation of the  $\text{TiCl}_4$ -(1) system resulted in a series of dark yellow to green complexes of varying composition<sup>17</sup> (suggestive of partial hydrolysis and/or reduction).

Reaction with  $\text{VCl}_3$  gave an insoluble chocolate-brown solid approximating to  $\text{VCl}_3 \cdot 0.5\text{CH}_2(\text{NMe}_2)_2$ . The 1 : 1 complex, isolated indirectly from the reduction of  $\text{VCl}_4$  with  $\text{B}_2(\text{NMe}_2)_4$ , has been interpreted as a monomeric five-co-ordinate vanadium(III) species with bidentate (chelate) ligand attachment.<sup>16</sup> Infrared spectral data for  $\text{VCl}_3 \cdot 0.5\text{CH}_2(\text{NMe}_2)_2$  indicate both unidentate (1368, 1063, 1045  $\text{cm}^{-1}$ ) and bidentate (1040, 1024, 998, 974, 963  $\text{cm}^{-1}$ ) ligand attachment. The pattern of  $\nu(\text{VCl})$  bands (387, 350, 315, 277  $\text{cm}^{-1}$ ) resembles that of the brown compound  $\text{VCl}_3 \cdot \text{NMe}_3$  and implies bridging halogen.<sup>18</sup> Mixing of  $\text{VCl}_3 \cdot 0.5\text{CH}_2(\text{NMe}_2)_2$  with neat pyridine (py) gives total ligand replacement with formation of the mauve  $\text{VCl}_3 \cdot 3\text{py}$ .<sup>19</sup> As a direct comparison, the donor behaviour of the phosphorus analogue  $\text{CH}_2(\text{PPh}_2)_2$  (dpm) with  $\text{TiCl}_4$  was also investigated. Dropwise addition of dpm to an equimolar amount of  $\text{TiCl}_4$  in benzene solution gave the bright orange 1 : 1 complex. Intense  $\nu(\text{TiCl})$  bands at 388, 380, 345, and 320  $\text{cm}^{-1}$  support an expected *cis*-octahedral ( $C_{2v}$ ) structure (Figure 1). Bands at 469 and 416  $\text{cm}^{-1}$  are assigned as  $\nu(\text{Ti}-\text{P})$  stretching modes.<sup>20</sup> The  $^1\text{H}$  n.m.r. spectrum shows the methylene protons at  $\delta$  3.73 [ $J(^{31}\text{P}-^1\text{H})$  6.6 Hz] and the ring protons at  $\delta$  6.4–6.8 (complex multiplet). The observed increase in the P–H coupling constant [ $J(^{31}\text{P}-^1\text{H})$  2.0 Hz, dpm] reflects the increased *s* character in the P–C bonds following P donation; the drastic change in the aromatic region profile,  $\delta$  7.41 (*meta*) and  $\delta$  7.21 (*ortho* and *para*) multiplets (dpm), could well suggest deviation from a planar  $\text{TiP}_2\text{C}$  configuration with non-equivalent phenyl groups. Chelation of dpm [and also the arsenic analogue  $\text{CH}_2(\text{AsPh}_2)_2$ ] often results in significant displacement of the methylene group from the  $\text{MP}_2$  plane.<sup>21</sup>

$\text{SiMe}_2(\text{NMe}_2)_2$ , (2).—Dropwise addition (273 K) of (2) to equimolar quantities of  $\text{MX}_4$  ( $\text{M} = \text{Zr}, \text{Hf}, \text{or Sn}, \text{X} = \text{Cl}; \text{M} = \text{Sn}, \text{X} = \text{Br}$ ) in benzene solution gave immediate precipitation of the appropriate 1 : 1 complexes. Increasing the ligand : metal ratio does not result in further complexation. The white solids were extremely air- and moisture-sensitive and showed a general insolubility in organic solvents. The one exception,  $\text{SnCl}_4 \cdot \text{SiMe}_2(\text{NMe}_2)_2$ , was somewhat soluble in benzene,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$  and could be recrystallised in low yield from the latter; additionally, it sublimes *in vacuo* (403–410 K) without apparent change.

Under similar conditions, the reaction of (2) with  $\text{TiCl}_4$  gave a pale yellow precipitate which on standing even at 273 K fairly rapidly turned to a green solid.

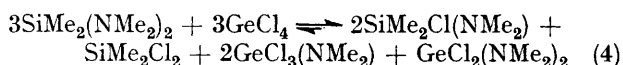
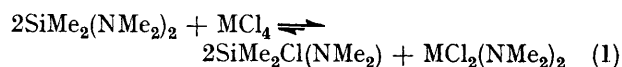
Subsequent work-up yielded dark green crystals of  $[\text{TiCl}_3(\text{NMe}_2)]$  and  $\text{SiMe}_2\text{Cl}(\text{NMe}_2)$ , b.p. 380 K (760 mmHg\*). We were able to successfully isolate pure samples of the yellow 1 : 1 complex on changing to the less polar *n*-hexane as solvent (273 K). Inevitably contamination with  $[\text{TiCl}_3(\text{NMe}_2)]$  slowly sets in however, even with samples stored in glass ampoules under a nitrogen atmosphere (273 K). Repeating the reaction with a two-fold excess of (2) again gives  $\text{SiMe}_2\text{Cl}(\text{NMe}_2)$  as the sole silicon-containing product together with a chocolate-brown solid approximating to  $[\text{TiCl}_2(\text{NMe}_2)_2]$ . The  $^1\text{H}$  n.m.r. spectrum shows a complicated pattern for *N*- $\text{CH}_3$  protons, including an intense broad resonance at  $\delta$  3.5, a paramagnetic titanium(III) species perhaps. Quite possibly this is identical with the non-stoichiometric product noted by Bürger and Neese<sup>22</sup> from the reaction of  $\text{TiCl}_4$  and  $\text{SiMe}_3(\text{NMe}_2)$ . Pure  $[\text{TiCl}_2(\text{NMe}_2)_2]$  is reported as brown crystals from the disproportionation of  $\text{TiCl}_4$  and  $\text{Ti}(\text{NMe}_2)_4$ .<sup>23</sup> The reaction between (2) and  $\text{CrCl}_3 \cdot 2\text{NMe}_3$  in benzene solution resulted in formation of the decomposition product  $\text{Cr}_2\text{Cl}_6(\text{NMe}_3)_3$ .<sup>24</sup> With  $\text{VCl}_3 \cdot 3\text{MeCN}$ , ligand exchange occurred but the resulting mauve vanadium(III) species proved to be non-stoichiometric.

A *cis*-octahedral ( $C_{2v}$ ) structure (Figure 1) is proposed for the series  $\text{MCl}_4 \cdot \text{SiMe}_2(\text{NMe}_2)_2$ . The i.r. spectra of the complexes show a conspicuous similarity; the major variations from that of the free ligand occur in the 500–900  $\text{cm}^{-1}$  region, reflecting the change in Si–N bonding following complexation. Intense metal–halogen stretching bands were observed at 340, 328, 320, 260  $\text{cm}^{-1}$ ,  $\nu(\text{SnCl})$ ; 417, 405, 365, 322  $\text{cm}^{-1}$ ,  $\nu(\text{TiCl})$ ; 344, 311  $\text{cm}^{-1}$ ,  $\nu(\text{ZrCl})$ ; and 342, 313  $\text{cm}^{-1}$   $\nu(\text{HfCl})$ .  $\text{SnBr}_4 \cdot \text{SiMe}_2(\text{NMe}_2)_2$  shows one broad and intense band at 210–220  $\text{cm}^{-1}$   $\nu(\text{SnBr})$ . Proton n.m.r. data ( $\delta$ ) are limited (solubility) to  $\text{SnCl}_4 \cdot \text{SiMe}_2(\text{NMe}_2)_2$  [0.36(6) ( $\text{SiCH}_3$ ), 2.19(6), 2.17(6) ( $\text{NCH}_3$ )];  $\text{SnBr}_4 \cdot \text{SiMe}_2(\text{NMe}_2)_2$  [0.38(6) ( $\text{SiCH}_3$ ), 2.14(6), 2.12(6) ( $\text{NCH}_3$ )]; and  $\text{ZrCl}_4 \cdot \text{SiMe}_2(\text{NMe}_2)_2$  [0.37(6) ( $\text{SiCH}_3$ ), 2.15(6), 2.09(6) ( $\text{NCH}_3$ )]. Uncomplexed ligand (2) shows singlets at  $\delta$  0.10(6) ( $\text{SiCH}_3$ ) and 2.45(12) ( $\text{NCH}_3$ ). Each complex shows a sharp doublet for the  $\text{NMe}_2$  protons at room temperature; these are temperature dependent with decay to a broad singlet on increasing the temperature (373 K). For a five-co-ordinate metal geometry (Figure 2) the separate donor and ‘dangling’  $\text{NMe}_2$  sites would account for the doublet. Raising the temperature would increase the exchange rate between free and bound sites, until in the fast-exchange limit the two signals coalesce. Alternatively, a six-co-ordinate metal geometry (Figure 1) could give non-equivalent  $\text{NMe}_2$  groups as a result of non-planarity of the equatorial  $\text{MX}_2\text{SiN}_2$  plane. Rapid inversion of the chelate ring at higher temperature averages out the different sites causing collapse to a single resonance. On balance, the latter model is favoured, *i.e.* the likelihood that the solid-state structure persists in solution fits in with the known preference for six-co-ordination for  $\text{M}^{\text{IV}}$ .

Direct mixing of (2) and  $\text{MCl}_4$  ( $\text{M} = \text{Si}$  or  $\text{Ge}$ ) in various

\* Throughout this paper : 1 mmHg  $\approx$  13.6  $\times$  9.8 Pa.

molar ratios either in benzene solution or as neat solutions gave rise to the exchange reactions (1)–(4). Exchange between  $MCl_2(NMe_2)_2$  and  $MCl_4$  ( $M = Si$  or  $Ge$ ) was also studied, equation (5).



All reactions were noticeably exothermic, to give clear colourless solutions. Products, which in each case

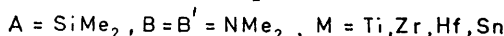
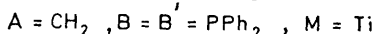
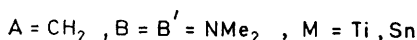
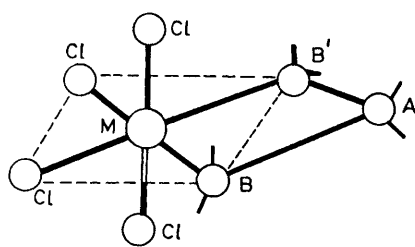


FIGURE 1 Six-co-ordinate geometry of the compounds  $MCl_4 \cdot ABB'$

remained unchanged after thermostating at 313 K for 24 h, were identified by chemical-shift comparisons with data from samples prepared independently:  $SiMe_2(NMe_2)_2$   $\delta$  2.48 ( $NCH_3$ ), 0.1 ( $SiCH_3$ );  $SiMe_2Cl(NMe_2)$   $\delta$  2.35

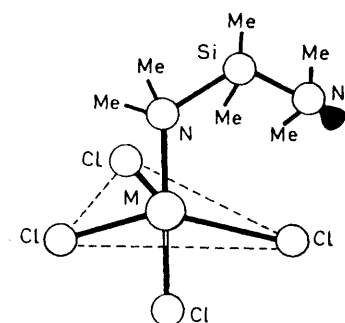
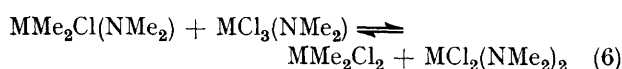


FIGURE 2 Five-co-ordinate geometry of the compounds  $MCl_4 \cdot SiMe_2(NMe_2)_2$

( $NCH_3$ ), 0.33 ( $SiCH_3$ );  $SiMe_2Cl_2$   $\delta$  0.40 ( $SiCH_3$ );  $SiCl_3(NMe_2)$   $\delta$  2.18 ( $NCH_3$ );  $SiCl_2(NMe_2)_2$   $\delta$  2.42 ( $NCH_3$ );  $GeCl_3(NMe_2)$   $\delta$  2.23 ( $NCH_3$ );  $GeCl_2(NMe_2)_2$   $\delta$  2.42 ( $NCH_3$ ). Sharp singlets were observed throughout, there being no evidence for line broadening as noted for some german-

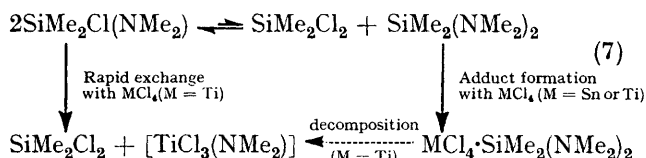
ium systems.<sup>25</sup> Peak height integration confirmed the overall stoichiometries.

Substituent exchange on silicon has been widely studied<sup>26,27</sup> and for halide- $NMe_2$  systems exchange is usually rapid and complete for any given ratio of reactants.<sup>28</sup> The systems studied [equations (1)–(5)] show no observable back reaction. One point of interest concerns the 1:1 reactions involving  $MCl_4$  and (2) ( $M = Si$  or  $Ge$ ). Whereas exchange of  $NMe_2$  groups is complete in the case of silicon [equation (3)], the corresponding reaction with germanium [equation (4)] leads to a mixture of products arising from simple combination of the 2:1 and 1:2 reactions respectively. To accord with these observations we might have expected the position of equilibrium for the direct reaction of  $MMe_2Cl(NMe_2)$  and  $MCl_3(NMe_2)$  [equation (6)] to lie to the right for  $M = Si$



but to the left for  $M = Ge$ . In both cases however, reaction was rapid and complete.

Dropwise addition of a two-fold excess of  $SiMe_2Cl(NMe_2)$  to  $SnCl_4$  in benzene gave (3 d) colourless crystals of  $SnCl_4 \cdot SiMe_2(NMe_2)_2$  (Figure 1). Work-up of the remaining solution afforded  $SiMe_2Cl_2$  as the sole silicon-containing product. A similar reaction using  $TiCl_4$  in n-hexane gave a brown solution which on standing (24 h) slowly deposited green crystals of  $[TiCl_3(NMe_2)]$ ;  $SiMe_2Cl_2$  was again recovered from the residual solution.

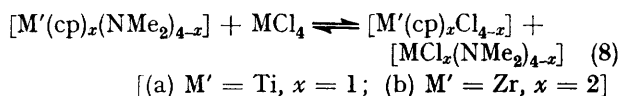


The slow formation of the  $SnCl_4 \cdot SiMe_2(NMe_2)_2$  adduct is in accord with the equilibrium position for the proposed disproportionation of  $SiMe_2Cl(NMe_2)$  lying well to the left [equation (7)]. Direct treatment of  $SiMe_2Cl_2$  and  $SiMe_2(NMe_2)_2$  gives an exothermic and rapid reaction from which  $SiMe_2Cl(NMe_2)$  was isolated in essentially quantitative yield. Formation of the titanium product  $[TiCl_3(NMe_2)]$  can be viewed either as a direct result of a rapid exchange reaction or *via* breakdown of  $TiCl_4 \cdot SiMe_2(NMe_2)_2$ . The facile decomposition of the latter compared with the tin(IV) analogue has been described above.

$[TiCl_3(NMe_2)]$ ,  $[Ti(cp)(NMe_2)_3]$ , (3), and  $[Zr(cp)_2(NMe_2)_2]$ , (4).—Dissolution of  $[TiCl_3(NMe_2)]$  in thf (tetrahydrofuran) or MeCN (solvent molecules, L) gives deep green solutions which on treatment with equimolar  $MCl_4$  ( $M = Si$  or  $Ge$ ) provide the pale yellow bis adducts  $TiCl_4 \cdot 2L$ . The rapid exchange:  $[TiCl_3(NMe_2)] + MCl_4 \rightleftharpoons TiCl_4 + MCl_3(NMe_2)$  provides  $TiCl_4$  which preferentially (to  $MCl_4$ ) gives complex formation with excess of L. The exact nature of the green  $[TiCl_3(NMe_2)]$ -thf, MeCN solutions, as distinct from the pale brown solutions formed in non-donor solvents, could not be

established. Removal of solvent reliably gave tarry non-stoichiometric materials. Addition of  $[\text{TiCl}_3(\text{NMe}_2)]$  to a two-fold excess of  $(\text{Me}_2\text{N})_3\text{P}=\text{O}$  (tdpo) in benzene solution gave a deep brown solution from which pale yellow crystals of *trans*- $\text{TiCl}_4 \cdot 2\text{tdpo}$ <sup>29</sup> slowly deposited (2 weeks). In the absence of halide exchange, the slow disproportionation  $2 [\text{TiCl}_3(\text{NMe}_2)] \rightleftharpoons [\text{TiCl}_2(\text{NMe}_2)_2] + \text{TiCl}_4$  is proposed as the initial rate-determining step.

The reactions of (3) and (4) with  $\text{MCl}_4$  ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Ti}, \text{Zr}, \text{or Hf}$ ) were investigated following direct mixing in benzene solution [equation (8)]. Work-up of the resulting solutions consistently gave (a)  $[\text{Ti}(\text{cp})\text{Cl}_3]$  and (b)  $[\text{Zr}(\text{cp})_2\text{Cl}_2]$  respectively to indicate group exchange as a general theme rather than *N*-donor chelation as observed in reactions with metal carbonyls.<sup>15</sup>



The identities of the dimethylamino-substituted metal(IV) chloro-species proved difficult to establish and, in several cases, changed somewhat with varying reaction conditions. For equimolar addition ( $\text{M} = \text{Si}$  or  $\text{Ge}$ ), removal of solvent followed by vacuum distillation gave (a)  $\text{MCl}(\text{NMe}_2)_3$  and (b)  $\text{MCl}_2(\text{NMe}_2)_2$ , respectively. With a large excess of  $\text{MCl}_4$ , however,  $\text{MCl}_3(\text{NMe}_2)$  was identified as the common 'second' product. For  $\text{M} = \text{Ti}$ , reaction (8b) produced a brown solid which gave a chocolate-brown sublimate identified as the non-stoichiometric form of ' $\text{TiCl}_2(\text{NMe}_2)$ '; reaction (8a) also gave a brown solid which resisted sublimation and whose  $^1\text{H}$  n.m.r. spectrum [ $\delta$  3.21 (singlet) with complex profile  $\delta$  2.0—3.7] indicated a complex mixture of  $\text{Ti}(\text{NMe}_2)$  species. A repeat of these reactions with a four-fold excess of  $\text{TiCl}_4$  provided green crystals of  $[\text{TiCl}_3(\text{NMe}_2)]$  as the 'second' product in both cases. Characterisation of the involatile solids formed as 'second' products in the remaining systems ( $\text{M} = \text{Sn}, \text{Zr}, \text{or Hf}$ ) proved inconclusive.

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